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Nuclear Chemistry

K-Shell Internal Ionization Accompanying Beta Decay. Y. Isozumi and S. Shimizu. *Phys. Rev. C*, 4, 522 (1971).—Internal ionization in the K shell during nuclear β decay has been studied experimentally as well as theoretically. The subsequent K x rays were measured in coincidence with emitted electrons for various segments of the β spectra of ^{147}Pm and ^{63}Ni , using 4π detection geometry for these electrons; the sources were mounted in the electron detectors. The energy-dependent ionization probability $P_K(E_\beta^0)$ was measured as a function of E_β^0 , where the parameter E_β^0 is defined as a sum of energies of the β particle and emitted K electron plus the K -shell binding energy of the daughter atom. This energy-dependent and the simultaneously measured total ionization probabilities have been found to be in fairly good agreement with theoretical values calculated by the theory developed based on a relativistic one-step treatment of electron shakeoff. From this result it has been established that electron shakeoff is the predominant mechanism even for electrons (β particles and K electrons) emitted with very low energies. As to the total ionization probability, it is pointed out that the theoretical values calculated by the simple wave-function-overlap theory using self-consistent-field wave functions should be improved by multiplying by a correction factor, a function of B_K and E_0 , where B_K is the K -shell binding energy of the daughter atom and E_0 is the ordinary maximum kinetic energy of β rays. The theoretical treatment of the phenomenon and future fruitful experiments to be hoped for are also discussed.

Dilute ^{57}Co Mössbauer Study on a Ferromagnetic Ni-Cu Alloy near the Transition Temperature. S. Nasu, Y. Murakami and R. Katano. *Phys. Letters*, 36A, 117 (1971).—Temperature dependence of the ^{57}Fe Mössbauer spectra in a ferromagnetic $\text{Ni}_{0.69}\text{Cu}_{0.31}$ alloy was measured. The analysis of hyperfine field distributions in the vicinity of the transition temperature provides a clue to elucidate the clustering and/or concentration fluctuation in this alloy system.

A Pulse Shape Discriminator for an X-Ray Proportional Counter and its Application to a Coincidence Experiment. Y. Isozumi and S. Isozumi. *Nucl. Instr. and Meth.*, 96, 317 (1971).—A pulse shape discrimination system has been developed for an x-ray proportional counter to reduce the background caused by high energy radiations, by the use of a modified time-to-pulse-height converter. Test measurements with argon filled counters have shown that the

system is at least 90% effective in reducing the background in the energy range 6~15 keV, while more than 95% of all the x-ray signals can be accepted. Even in the 20~35 keV region, reasonably good results for the background reduction and the x-ray acceptance have also been obtained. The technique has been successfully applied to the coincidence experiment with two proportional counters in order to eliminate false coincidence due to unfavourable high energy radiations passing through both counters.

The (p, pd) Reaction to Investigate the Nucleon-Nucleon Correlations in the Nucleus. N. Fujiwara. *Genshikaku Kenkyu*, **15**, 55 (1970), in Japanese.—It is well known that the deuteron yield from various nuclei are fairly large when the nucleus are bombarded by some hundred MeV protons. The deuteron production mechanism are discussed by several authors and the quasi-free p-d scattering in the nuclei are proved to be dominant. In this report, the author will point out the feasibility of the (p, pd) reaction at high energy region as a tool to investigate the nucleon-nucleon pairing correlations, when kinematically complete experiment is done.

Analytical Chemistry

Fluorometric Determination of Cerium in Sea-water. T. Shigematsu, Y. Nishikawa, K. Hiraki, S. Gōda and Y. Tsujimoto. *Japan Analyst*, **20**, 575 (1971), in Japanese.—Cerium in sea-water was determined by the Ce (IV)~Ce (III) fluorometric method.

Into 20 l of sea-water were added 100 ml of conc. HCl and 50 mg (30 mg, 10 mg, 10 mg) of Fe^{3+} as FeCl_3 solution, and pH of the solution was adjusted to 9~9.5. After standing overnight, the precipitate was filtered and dissolved in 40 ml of 6N HCl. Fe^{3+} was extracted with 40 ml of MIBK, and the aqueous phase was evaporated to dryness with 3 ml of 70% HClO_4 . The residue was treated with 10 ml of 0.002N HClO_4 , poured on the column (HDEHPVC column) and eluted with 0.3N perchloric acid solution (flow rate: 1 ml/min). The cerium fraction of the eluant (50~100 ml) was decomposed with HClO_4 and evaporated again to dryness. The residue was dissolved with HClO_4 to make the final perchloric acid concentration 0.7N. The solution was transferred to a 25 ml volumetric flask with 500 μg of Ti^{3+} , and was diluted to the volume with water. The fluorescence intensity of the solution was measured at 350 nm with excitation at 255 nm. In this procedure, the recovery of cerium was about 90%.

Cerium in sea-water collected at offshore of Dōrinzawa, Tokyo and Shirahama, Wakayama was found to be $2\sim5\times10^{-3}$ $\mu\text{g/l}$.

Physical Chemistry

Dielectric Properties of Some Diols. E. Ikada. *J. Phys. Chem.*, **75**, 1240 (1971).—The dielectric properties of the four diols, 2-methyl-2,4-pentanediol, di-

propylene glycol, 2-ethyl-1,3-hexanediol, and thiodiglycol, were studied to correlate the dielectric properties with the molecular structures. The measurements of the dielectric constant and loss were carried out over the audio- and radio-frequency range at temperatures from -70 to 60° . All of these diols except thiodiglycol showed the Davidson-Cole-type dispersions. No significant difference concerning the molecular structure in the shape of the dielectric relaxations was observed for these rather complicated diols. The dielectric behavior of diols was discussed in contrast with those of polyamino compounds.

Studies on Built-up Films by Means of the Polarized Infrared ATR Spectrum.

1. Built-up Films of Stearic Acid. T. Takenaka, K. Nogami, H. Gotoh and R. Gotoh. *J. Colloid Interface Sci.*, **35**, 395 (1971).—The infrared attenuated total reflection (ATR) spectra of molecular layers of stearic acid built upon the germanium plate by the Blodgett method were studied by using the polarized radiations with the electric vectors parallel and perpendicular to the plane of incidence. It is concluded that the built-up films are made of an assembly of crystallites of the monoclinic system, and that the crystallites are oriented so that their crystallographical c -axis may form angles from *ca.* 27° to 35° with the z -axis (the axis perpendicular to germanium-stearic acid interface) depending upon the number of layers, but at random around the z -axis (uniaxial orientation with respect to the z -axis) irrespective of the direction of withdrawal of the plate in the film preparation. From penetration depth of the totally reflected radiation and changes in reflectivity with the numbers of layers, the thickness of a single monomolecular layer is estimated to be *ca.* 23.8 \AA , showing good agreement with the values previously proposed by Blodgett and by Müller.

Simultaneous Measurements of Stress and Infrared Dichroism on Polymers.

II. Continuous Elongation and Stress Relaxation of Polychloroprene. T. Takenaka, Y. Shimura and R. Gotoh. *Reports Progress Polymer Phys. Japan*, **14**, 357 (1971).—Simultaneous measurements of stress and infrared dichroism were made of polychloroprene (Neoprene Type AC) films during the course of continuous elongation at the constant rate $25\%/min$ and of stress relaxation at 400% elongation. The time dependence of the infrared dichroism was obtained by measuring the intensity change at fixed wavenumbers of absorption band maxima on the differential polarized infrared spectra. Both the degree of crystallinity of sample films and the orientation function of transition moments were calculated from the results of the infrared dichroic measurements under the assumption of uniaxial orientation.

In the continuous elongation experiments, it was found that the orientation functions for crystalline-sensitive bands showed maxima at 25% elongation and then decreased rapidly, changing their signs from positive to negative. There also appeared the yield point in the stress-strain curve and the beginning of sharp decrease of crystallinity at the same degree of elongation 25% . These facts were interpreted in terms of the orientation of the crystalline phase followed by the degradation of crystallites and drawing out of the molecular chain

from the crystallites. In the stress relaxation experiments, moderate changes in the orientation functions were found for various characteristic absorption bands. Little difference was observed between changes in the orientation functions for the amorphous and crystalline-sensitive bands. This makes a contrast with the previous results for vulcanized natural rubber, where the orientation of the crystalline phase was completed almost immediately after elongation, while in the amorphous phase the molecular chains were oriented gradually during the course of stress relaxation.

Infrared Dichroism and Orientation of Plasticizers in Stretched Polyvinylchloride Films. J. Umemura, T. Takenaka, S. Hayashi and R. Gotoh. *Reports Progress Polymer Phys. Japan*, **14**, 527 (1971).—Infrared dichroic measurements were made of stretched polyvinylchloride (PVC) films containing dioctyl phthalate and diethyl phthalate as plasticizer. It was concluded that dioctyl phthalate molecules added less than about 15% were oriented keeping their relative orientation to PVC chain constant, and that those added more than about 15% were dispersed freely in PVC medium. For the former case, the angles between PVC chain axis and three mutually orthogonal axes of benzene ring in phthalates were calculated from the orientation functions for the benzene absorption bands. The effect of alkyl chain length of phthalates on the orientation was discussed by comparing the results obtained for dioctyl phthalate and diethyl phthalate.

Studies of Monomolecular Films by Means of Infrared Spectroscopy. T. Takenaka. *Hyomen*, **8**, 636 (1970), in Japanese.—This is a review article of monomolecular films studied by means of infrared transmission spectra and attenuated total reflection (ATR) spectra. The latter method was emphasized as a new technique useful for studying thin surface films of molecular thickness. Discussions were made of three main topics; interaction between monomolecular films of acids and metal ions, secondary structure of polypeptides in monomolecular films, and molecular orientation in multilayer films.

Infrared and Raman Spectra. T. Takenaka, S. Hayashi and J. Umemura. *Japan Analyst (Annual Review)*, **19**, 41R (1970), in Japanese.—This is a review article dealing with the progress in the field of the infrared and Raman spectroscopies during the two-year period, 1969–1970. Of the numerous number of works reported in this period, 497 papers cited to indicate significant developments of infrared and Raman spectrophotometers, sample preparations, assignments of vibration bands, studies of group frequencies, studies of band intensities, application to the studies of intramolecular and intermolecular interactions, and application to the quantitative analysis. The growth of activity in the field of Raman spectroscopy, primarily due to the widespread application of gas lasers as light sources, was emphasized.

The Coalescence of Mercury Droplets in Mixed Solvents. M. Matsumoto. *J. Chem. Soc., Japan*, **91**, 708 (1970), in Japanese.—In order to study the influence of

the dielectric constant on the dispersion and coagulation in lyophobic dispersion systems, the range of electrical potential of coalescence was measured by using the twin dropping mercury electrodes immersed into mixed solvents (methanol-water) containing potassium chloride. The potential range of coalescence became large with the decrease of the dielectric constant, *i.e.* with the increase in methanol content. This behaviour could be explained by the increase in the ionic strength of the solution, *i.e.* the compression of the diffuse double layer. It was observed from measurements of differential double layer capacities that the dielectric constant in the diffuse double layer was small compared with the bulk value, being proportional to the third power of the dielectric constant in the Stern layer. It was found that the free energy of adsorption of methanol molecules at the mercury-solution interface was ca. -1 Kcal/mol., and hence the coalescence of mercury droplets was little influenced by the formation of the adsorbed film of methanol molecules.

The Mechanism of Coalescence of Liquid Droplets and the Stability of Disperse Systems. M. Matsumoto. *Hyomen*, 9, 266 (1971), in Japanese.—The influence of the surface potential, ionic strength, dielectric constant, and adsorption of surface active materials upon the coalescence of liquid droplets was studied as the model of stability of disperse systems. The coalescence experiment of liquid droplets was carried out by the twin dropping electrodes immersed in solutions of various compositions. The coalescence is governed by two mechanisms. The first is the electrostatic and van der Waals interactions between liquid droplets, and the second the protection due to the adsorption of surface active materials. The former was found when solutions contain inorganic or surface inactive organic electrolytes, and the latter was found when aqueous or oil phase contain surface active materials. It was concluded by using DLVO's theory that the coalescence could be explained on the basis of the overlapping of electrical double layer, the fundamental principle of the interaction between lyophobic colloids.

Linear Heisenberg Interaction in Stable Organic Free Radicals. J. Yamauchi, T. Fujito, H. Nishiguchi and Y. Deguchi. *Proceedings of the 12th International Conference on Low Temperature Physics, Kyoto*, 805 (1970).—To examine the magnetic interactions between unpaired electrons in organic free radicals, the susceptibilities and the electron spin resonance linewidths were measured at low temperatures. The data are shown to be generally consistent with a Heisenberg type isotropic interaction in one dimension and the effect of short range ordering of spins was found in the ESR linewidth.

Magnetic Ordering in a Linear Antiferromagnet, CsNiCl_3 . M. Mekata, K. Adachi, H. Takaki and N. Achiwa. *Proceedings of the 12th International Conference on Low Temperature Physics, Kyoto*, 801 (1970).—Single crystal neutron diffraction and specific heat measurements were carried out on CsNiCl_3 . Long range magnetic ordering with triangular spin structure was found below 4.6°K consistent with powder neutron diffraction results. Sublattice magnetization

follows a function with a critical exponent of 0.35 ± 0.05 near the transition temperature and extrapolates a value of $1.5 \pm 0.1 \mu_B$ at 0°K. Long range magnetic ordering entropy was only 5% of the total.

Neutron Diffraction Study of Antiferromagnetism in Face-Centered Cubic Mn-Ir Alloys. T. Yamaoka, M. Mekata and H. Takaki. *J. Phys. Soc. Japan*, **31**, 301 (1971).—This note reports the magnetic structure and the magnetic transition temperatures determined by single-crystal neutron diffraction experiments on the f.c.c. Mn-Ir alloys containing 10, 15 and 20 at. % Ir. The magnetic moment per Mn atom as well as the lattice parameters at room temperature remains almost constant over Ir-concentration range at least from 10 at. % to 20 at. %, and it may be concluded that Ir enhances remarkably the magnetic interaction in f.c.c. Mn.

Direct Observation of Phthalocyanine Molecules in Epitaxial Films. N. Ueda, T. Kobayashi, E. Suito, Y. Harada and M. Watanabe. *Microscopie Électronique*, **1**, 23 (1970).—By high resolution electron microscopy, the epitaxial thin film of hexadecachloro-Cu-phthalocyanine, whose crystal structure was determined on the basis of an optical transform analysis of electron diffraction was observed to show the clear image of individual molecules with quatre-foiled shape.

The molecules are found to be about 40 times more resistant to electron radiation damage than ordinary Cu-phthalocyanine indicating the possibility for the test specimen in the future molecular microscopy.

High Resolution Electron Microscopy on Very Small Colloidal Particles of Noble Metals. E. Suito, Y. Murata, N. Uyeda and M. Watanabe. *Microscopie Électronique*, **1**, 25 (1970).—High resolution electron microscopy was applied to gold and platinum sol particles, which assume various thin structures as revealed from the diffraction contrast moiré fringes and lattice images.

Electron Microscopy of Epitaxial Reaction of Organic Complex Crystals. N. Uyeda, T. Kobayashi and E. Suito. *Microscopie Électronique*, **2**, 433 (1970).—Tetracyanoquinodimethane (TCNQ) was found to form particular epitaxial films when evaporated on cleaved faces of alkali halide single crystal. It was also found that metals such as nickel, silver and aluminum, evaporated onto the TCNQ epitaxial films, diffused as ions to form corresponding charge transfer complexes, also assuming epitaxial relations to the original crystallites.

The Crystal Structure of the 2:3 Complex of Zinc Phthalocyanine and *n*-Hexylamine. T. Kobayashi, T. Ashida, N. Uyeda, E. Suito and M. Kakudo. *Bull. Chem. Soc. of Japan*, **44**, 2095 (1971).—Crystal of the 2:3 complex of zinc-phthalocyanine and normal hexylamine were studied. They are monoclinic, space group $P2_1/c$, with cell dimensions $a=12.40$, $b=15.76$, $c=20.05$, $\beta=93.2^\circ$ and there are four phthalocyanine and six hexylamine molecules per cell. The phthalocyanine molecule is not planar and central zinc ion is displaced from

the plane by 0.48 Å toward the nitrogen atom of the amine. Zinc ion is of a square pyramidal five coordination. There are two bonding states for the amine in the complex crystal. One is weakly bonded and can be easily released from the lattice and the other is strongly bounded and coordinated directly to the zinc ion. None of the atomic parameters of these amines except those of the coordinating nitrogen were exactly determined.

Thermal Transformation of Vacuum-Condensed Thin Films of Copper-Phthalocyanine. M. Ashida, N. Uyeda and E. Suito. *J. of Crystal Growth*, 8, 45 (1970).—Copper-phthalocyanine forms thin crystalline films of the metastable α -form with definite epitaxial orientations when vacuum-deposited onto a cleaved face of muscovite. The thermal transformation of these thin films into the stable β -form was observed by electron microscopy and electron diffraction. The transformed crystals show an epitaxial orientation with their (001) faces parallel to the substrate independent of the initial orientations. The B-form crystals grow as a long needle along its b-axis when it coincides with that of the original α -crystals, while the β -form crystals appear as relatively short flakes when both b-axes show no coincidences at all. The mechanism of thermal growth is discussed on the basis of molecular arrangement from one crystal to another as well as the influence of the lattice structure of the substrate surface.

Lattice Image of Organo-Montmorillonite. E. Suito and T. Yoshida. *Nature Phys. Sci.*, 229, 22 (1971).—A set of two lattice images corresponding to (001) planes and (11) or (02) planes was observed at the curled edge of an organo-montmorillonite particle having an expanded layer structure caused by inter-layer adsorption of octadecylammonium.

Electron Microscopic Observation of Fine Structure of Cu_3Se_2 Crystals. H. Morikawa, M. Shiojiri and E. Suito. *J. of Applied Physics*, 42, 2144 (1971).—The fine structure having many zigzags and stripes was observed in the (110) plane of the thin film of a Cu_3Se_2 . The zigzags are composed of rectangles, which show various contrast depending on diffraction condition. The strips are parallel to the [110] direction and the periodicity is greater than several tens angstroms.

These fine structures are assumed to be due to planar defects caused by nonstoichiometry of the crystals. The lattice image of 3.11, 4.27 and 4.53 Å was observed by high resolution electron microscope.

Freeze Drying Technique in the Study of the Fabric of Moist Clay Sediment. Neal O'Brien, M. Arakawa and E. Suito. *J. of Electron Microscopy*, 19, 277 (1970).—Using a new technique of freeze drying, the scanning electron micrograph of the fabric of uncompressed flocculate Seto-clay was showed. The most apparent feature was the porous open texture and the random arrangement of irregularly shaped flakes.

The Fluidity and Structure of Powder Bed in a Vibrating State. M. Arakawa

and M. Nishino. *J. of the Society of Materials Science, Japan*, **20**, 776 (1971), in Japanese.—The structure of powder bed in a vibrating state of various graphite of different particle sizes has been discussed on the bases of variation of electric resistance of powder bed with the vibration intensity. The fluidity measurements were made with a rotary type viscometer.

The relations between the amplitude and electric resistance or fluidity of powder bed are similar to the change found in the relation of temperature *vs.* specific volume in glass transition of various materials.

The Effect of Water on the Cohesion of Particles. M. Nishino and M. Arakawa. *J. of the Society of Materials Science, Japan*, **20**, 781 (1971), in Japanese.—In order to investigate the effect of water on the cohesion of powder, the experiments were made with a system composed of spherical glass powders, water and benzene. In these systems, the adsorption weight of water, sedimentation volumes and angles of repose were measured. From the results, it was considered that the water was uniformly adsorbed on the surfaces of particles first, and then was condensed at the contact points between the particles and formed the water bridges. In the later range, sedimentation volumes and angles of repose decreased with increase of the adsorption weight of water, showing the same tendency as the theoretical attractive force due to the liquid bridge between the two spherical particles.

Electron Microscopic Investigations of Powders —The shape, crystal habit and microstructure of fine particles—. E. Suito (Supervisory Editor: H. Yukawa). *Profiles of Japanese Science and Scientists Kodansha Ltd.*, 245 (1970).—A review: Shape of primary particles and composite particles, crystal habit, ultra-thin sectioning of particles, microstructure and crystal lattice structure of particles were shown with many electron micrographs.

The Principle of Crystal Growth of Powderly Materials. N. Uyeda. *Color materials*, **43**, 612 (1970), in Japanese.—A review: The nucleation and growth of precipitates in solution were discussed. Some practical examples were also referred to in regard to various organic pigments.

Inorganic Chemistry

Microstructure and Strength of Crystallized Glass of Photoceram-Type. Y. Utsumi. *Yogyo-Kyokai-Shi*, **79**, 20 (1971).—Microstructure and bending strength of a photoceram-type crystallized glass of the composition SiO_2 81, Li_2O 12.5, K_2O 2.5, Al_2O_3 4, CeO_2 0.03, Au 0.027% in weight were studied with a particular attention to its surface structure. The results are summarized as follows;

1) The surface of both the samples heated up to 620°C and up to 900°C had a structure different from the interior. In the former lithium disilicate crystals were precipitated at the surface of the sample in addition to lithium metasilicate which was the only crystalline phase found in the interior. The lithium disilicate

crystals were oriented with the (002) plane parallel to the surface. In the latter the crystalline phases were lithium disilicate and α -quartz throughout the sample, but the lithium disilicate crystals oriented themselves at the surface.

2) The bending strength of the crystallized glasses obtained by heating up to 620°C was independent of the size of crystals found in the interior, before removing the surface layer, while it increased with decreasing grain size after the original surface layer was removed.

3) The strength of the crystallized glasses obtained by heating up to 900°C was intimately related to the size of crystal grains precipitated in the interior both before and after removal of the original surface layer; the strength increased with decreasing grain size. Presence of the strength-grain size relationship for the samples before removal of the original surface layer was explained by the fact that the length of the oriented crystals at the surface decreased with the grain size in the interior. The strength-grain size relationship for the samples after removal of the surface layer was explained by Orowan's theory on polycrystalline materials.

Glasses with Heterogeneous Structure. S. Sakka. *Oyo-Butsuri*, 40, 63 (1971), in Japanese.—Various physical properties of newly developed phase separated glasses, crystallized glasses, photosensitive glasses and photochromic glasses have been described.

Applications of Glass-Ceramics. S. Sakka. *Kinzoku*, June 15, 49 (1971), in Japanese.—Developments in the field of glass-ceramics have been reviewed with emphasis on composition and nucleation agent, strengthening of glass-ceramics, sealing of glass-ceramics with metals, glasses and ceramics and application to daily utensils and industrial devices.

Phase Separation and Crystallization of Glasses their Application. S. Sakka. *Kagaku-to-Kogyo (Science and Industry)*, 45, 73 (1971), in Japanese.—Processes of phase separation and crystallization, various properties of phase-separated and crystallized glasses and their application have been discussed.

Relation between Apparent Glass Transition Temperature and Liquidus Temperature for Inorganic Glasses. S. Sakka and J. D. Mackenzie. *Journal of Non-Crystalline Solids*, 6, 145 (1971).—The ratio of the glass transition temperature T_g to the liquidus temperature T_l (or T_m) was calculated for a wide variety of inorganic glass forming systems including the elements, oxides and sulfides and technologically important systems such as borates and silicates. It was found that a simple empirical rule $T_g/T_l = 2/3$ which was suggested for organic polymers holds surprisingly well for inorganic systems. The rule was applied to identify so called amorphous substances as glass.

Role of CaO and SiO₂ in Sintering of Manganese Zinc Ferrite. Y. Bando, Y. Ikeda, T. Akashi and T. Takada. *Modern Developments in Powder Metallurgy*, 4, 339 (1971).—It was reported that the discontinuous grain growth in sintering

of manganese zinc ferrite was caused by simultaneous addition of minor amounts of CaO and SiO₂ and explained by liquid phase sintering. Liquid formation in the system Mn_{0.5}Zn_{0.5}Fe₂O₄-CaO-SiO₂ and wettability of the ferrite with liquid were experimentally examined. The liquid temperature of the three components system was studied and the formation of liquid phase above 1100°C was confirmed. There was one eutectic at 30 mole % CaO, 60 mole % SiO₂ and 10 mole % ferrite. Wettability of the ferrite with the liquid was investigated by an infiltration method. The sintered ferrite was infiltrated by the liquid. Its microstructure showed that the liquid penetrated grain boundaries; namely the glassy phase existed at grain boundaries. Such a glassy phase was observed in the sintered ferrite containing only 1 wt % of CaO and SiO₂. These observations suggest that the liquid phase sintering occurred during heating of the ferrite containing CaO and SiO₂.

Electrical Properties of V₈O₁₅ Single Crystals. H. Okinaka, K. Kosuge, S. Kachi, K. Nagasawa, Y. Bando and T. Takada. *Phys. Letters*, **33A**, 370 (1971).—This is the first report on electrical properties of V₈O₁₅ single crystals. Above 70°K (Tt) V₈O₁₅ is metallic and shows a sharp increase in resistivity of a factor of 10 at Tt. Below Tt V₈O₁₅ is semiconducting and an activation energy gradually decreases with decreasing temperature. Tt agrees with one obtained from magnetic susceptibility measurement.

Growth and Magnetic Properties of V₈O₁₅ Single Crystals. K. Nagasawa, Y. Bando, T. Takada, H. Horiuchi, M. Tokonami and N. Morimoto. *Japan J. appl. Phys.*, **9**, 841 (1970).—This note reports on the preparation of single crystals of V₈O₁₅ by chemical transport reaction method, on the phase identification of V₈O₁₅ by means of the x-ray precession method and on the magnetic properties.

Electron Diffraction Study on the "Shear Structure" of V_nO_{2n-1}. K. Kosuge, H. Okinaka, S. Kachi, K. Nagasawa, Y. Bando and T. Takada. *Japan J. appl. Phys.*, **9**, 1004 (1970).—Samples used in this experiment were powders prepared by ordinary method or single crystals prepared by chemical transport reaction. The results from the analysis of a large number of diffraction patterns of follows; (1) In all diffraction patterns, the spots due to the superstructure is found along *g* {121}. (2) The phase from *n*=4 to 9 were confirmed to be one phase. Observations for samples VO_{1.95} and VO_{1.933} showed that these were mixtures of V₉O₁₇ and VO₂. The structure corresponding to *n*≥10 was not found out.

The Chemical Transport Reaction of Spinel-type Oxides. K. Nagasawa, Y. Bando and T. Takada. *Bull. Chem. Soc. Japan*, **44**, 1577 (1971).—Single crystals and thin films of spinel-type oxides were prepared by a chemical transport reaction in a closed system, using HCl gas as the transport agent. This paper reports on the preparation conditions and the reaction process of the chemical transport reaction. The reaction process of Co₃O₄ was found to be different from that of other oxides, since Co₃O₄ was dissociated into CoO and O₂ in the

closed tube. The reaction process was explained by the difference in the dissociated oxygen pressure between the source zone and the crystallization zone in the system. The chemical transport reaction of NiFe_2O_4 was applied to the preparation of thin film. The single crystal thin film were epitaxially grown on the (110) and (111) surfaces of MgO .

Electrical Properties of V_6O_{11} and V_7O_{13} Single Crystals. H. Okinaka, K. Nagasawa, K. Kosuge, Y. Bando, S. Kachi and T. Takada. *J. Phys. Soc. Japan*, **27**, 245 (1970).—Above 177°K (Tt) V_6O_{11} is metallic, and shows a sharp increase in resistivity of a factor of 10^4 at Tt. Below Tt it is semiconducting, with an activation energy of about 0.12 eV. V_7O_{13} metallic throughout the temperature range from 4.2°K to room temperature without phase transition. The temperature dependence of the thermoelectric power was measured on V_6O_{11} and V_7O_{13} single crystals.

Properties of Ti_4O_7 Single Crystals. K. Nagasawa, Y. Kato, Y. Bando and T. Takada. *J. Phys. Soc. Japan*, **29**, 241 (1970).—The single crystals of Ti_4O_7 were prepared by chemical transport reaction. Susceptibility and electrical resistivity were measured on single crystals and had a marked kink at 150°C . The transformation at 150°C seems to be from paramagnetic to paramagnetic property and is semiconductor to metal transition.

Magnetic Properties of $\alpha\text{-NaFeO}_2$. T. Ichida, T. Shinjo, Y. Bando and T. Takada, *J. Phys. Soc. Japan*, **29**, 795 (1970).—It was found that $\alpha\text{-NaFeO}_2$ is an antiferromagnet with the Neel temperature of 11 K and the internal magnetic field at 4.2 K was 455 KOe.

Mössbauer Study of Fe_2TiO_5 and FeTi_2O_5 . S. Muranaka, T. Shinjo, Y. Bando and T. Takada. *J. Phys. Soc. Japan*, **30**, 890 (1971).—Mössbauer effect and magnetic susceptibility measurements on Fe_2TiO_5 and FeTi_2O_5 are reported. The internal field of Fe_2TiO_5 at 4.2 K was 310 kOe. For FeTi_2O_5 , the internal field at 4.2 K was 190 kOe and the maximum of the susceptibility was observed at 7 K.

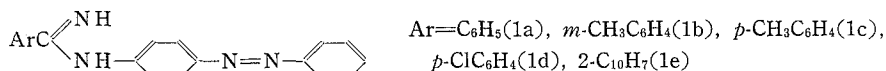
On the Spin Arrangement in “Kagome” Lattice of Antiferromagnetic $\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$. M. Takano, T. Shinjo and T. Takada. *J. Phys. Soc. Japan*, **30**, 1049 (1971).—Experimental results showed that $\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$ is antiferromagnetic below 60°K and in each crystal c-plane, Fe ions form a compensated antiferromagnet. The crystal structure of Fe ions in the c-plane is a “kagome” lattice and it has been known that collinear spin arrangements are not stable in the kagome lattice. An estimation of the spin structure was attempted with the analysis of the Mössbauer spectrum and a kind of triangular configuration was suggested.

Mössbauer Effect Study of KFeO_2 T. Ichida, T. Shinjo, Y. Bando and T. Takada. *J. Phys. Soc. Japan*, **29**, 1109 (1970).—Reported in this note is the result of the Mössbauer measurements on potassium orthoferrite, KFeO_2 , in a wide

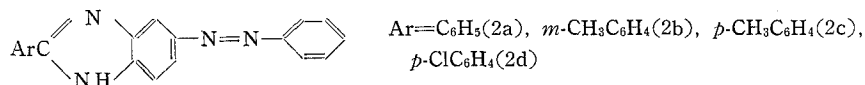
temperature range between 80 K and 993 K. The Neel temperature of KFeO_2 was found to be an extremely high value, 983 K.

Organic Chemistry

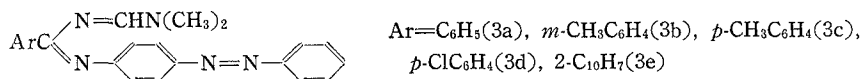
Synthesis and Reaction of Amidine Having Azo Group. T. Ishibashi, S. Tanimoto and M. Okano. *Yuki Gosei Kagaku Kyokai Shi*, **29**, 421 (1971), in Japanese.—The condensation of aromatic nitriles with 4-aminoazobenzene by AlCl_3 gave the following amidines having azo group; N-(4-phenylazo) phenylbenzamidinium (1a), N-(4-phenylazo) phenyl-*m*-toluamidinium (1b), N-(4-phenylazo) phenyl-*p*-toluamidinium (1c), *p*-chloro-N-(4-phenylazo) phenylbenzamidinium (1d) and N-(4-phenylazo) phenyl-2-naphthamidinium (1e).



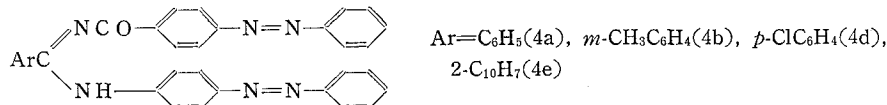
The HCl-adducts of the above amidines were converted into the corresponding 2-aryl-5-phenylazobenzimidazole [(2a), (2b), (2c) and (2d)] by N'-chlorination by sodium hypochlorite and the subsequent dehydrochlorination by NaHCO_3 .



Upon treatment with N,N-dimethylformamide dimethylacetal, the above amidines gave the corresponding N-dimethylaminomethylidene-N'-(4-phenylazo) phenylamidinium [(3a), (3b), (3c), (3d) and (3e)].



The corresponding N'-(4'-phenylazo) benzoyl-N-(4-phenylazo)-phenylamidinium [(4a), (4b), (4d) and (4e)] were also obtained by the condensation of *p*-phenylazobenzoyl chloride with the aid of NaHCO_3 .



(1a), (1b), (1c), (2a), (2b), (2c), (3a), (3b), (3c), (4b) and (4d) dyed acetate fiber yellow or light yellow.

Reactions of the Grignard Reagents Prepared from 4-Chloro-2,5-dimethylstyrene and 4-Chloro-2,5-dimethyl- α -methylstyrene. S. Tanimoto, Z. Mouri and M. Okano. *Yuki Gosei Kagaku Kyokai Shi*, **29**, 313 (1971), in Japanese.—4-Chloro-2,5-dimethylstyrene (3a) was easily obtained by dehydration of 4-chloro-2,5-dimethylphenylmethylcarbinol (2a) prepared by the action of 4-chloro-2,5-dimethylphenylmagnesium chloride on acetaldehyde.

Instead of acetaldehyde, the reaction was carried out with acetone, in which

case the product was 4-chloro-2,5-dimethyl- α -methylstyrene (3b).

2,5-Dimethyl-4-vinylbenzoic acid (4) 2,5-dimethyl-4-(N,N-dimethylaminomethyl) styrene (6a), 4-(N,N-diethylaminomethyl)-2,5-dimethylstyrene (6b) and 2,5-dimethyl-4-(N,N-di-*n*-propylaminomethyl) styrene (6c) were synthesized by the addition of the Grignard reagent prepared from (3a) to carbon dioxide, N,N-dimethylaminomethyl-*iso*-butyl ether, N,N-diethylaminomethyl-*n*-butyl ether and N,N-di-*n*-propylaminomethyl-*n*-butyl ether, respectively.

(4), (6a), (6b) and (6c) could be polymerized in the presence of 2,2'-azobisisobutyronitrile.

When the Grignard reagent prepared from (3b) was used, the resulting products were 2,5-dimethyl-4-(N,N-dimethylaminomethyl)- α -methylstyrene (8a), 4-(N,N-diethylaminomethyl)-2,5-dimethyl- α -methylstyrene (8b) and 2,5-dimethyl-4-(N,N-di-*n*-propylaminomethyl)- α -methylstyrene (8c).

Syntheses of Acrylamide Derivatives in the Ritter Reaction. S. Tanimoto, M. Kimura and M. Okano. *Yuki Gosei Kagaku Kyokai Shi*, 28, 1035 (1970), in Japanese.—This paper describes the results obtained in applying the Ritter reaction to syntheses of N-substituted acrylamides. N-[1-(*p*-chlorophenyl) ethyl] acrylamide (1a), N-[1-(*p*-chlorophenyl) isopropyl] acrylamide (1c) and N-[1-(*p*-chlorophenyl)-1-methylpropyl] acrylamide (1d) were prepared by the reaction of acrylonitrile and each one of *p*-chlorophenylmethylcarbinol, *p*-chloro- α , α -dimethylbenzyl alcohol and 2-(*p*-chlorophenyl)-2-butanol in the presence of concentrated sulfuric acid.

Similarly, N-[1-(*p*-chlorophenyl) ethyl] methacrylamide (1b) was prepared from methacrylonitrile.

When the reaction was carried out with N-(hydroxymethyl)-*p*-toluamide, N-(hydroxymethyl)-*p*-chlorobenzamide and N-(hydroxymethyl)-2-naphthamide, three methylene-bis-amides, *i.e.*, N-(*p*-toluamidomethyl) acrylamide (3e), N-(*p*-chlorobenzamidomethyl) acrylamide (3f) and N-(2-naphthamidomethyl) acrylamide (3h) were obtained.

Reaction of N-(hydroxymethyl) acrylamide with benzonitrile or with methacrylonitrile could be achieved, and N-benzamidomethylacrylamide (5) or N-acrylamidomethylmethacrylamide (6) was prepared.

Benzoyl peroxide catalyzed polymerization of (1a), (1b), (1c) and (1d) gave vinyl polymers.

Vinyl polymerization of (3e), (3f), (3h) and (5) were also investigated by potassium persulfate catalyst.

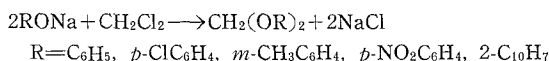
It was recognized that sodium tert-butoxide catalyzed polymer of (1a), (1d), (3f), (3h) and (5) were hydrogen migrated polymer at least predominantly.

Syntheses of Some Chloroepoxides Using α , β -Dichloropropionaldehyde. S. Tanimoto and S. Yasuda. *Yuki Gosei Kagaku Kyokai Shi*, 29, 530 (1971), in Japanese.—1-Chloro-2,3-epoxybutane (bp 62~63°C/82 mmHg, yield 27%), 1-chloro-2,3-epoxypentane (bp 46°C/18 mmHg, yield 39%), 1-chloro-2,3-epoxyhexane (bp 66.5~67°C/20 mmHg, yield 28.8%), 1-chloro-2,3-epoxyheptane (bp 81~81.5°C/19

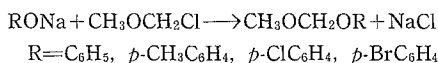
mmHg, yield 33.2%) and (3-chloro-1,2-epoxypropyl) benzene (bp 102~104°C/5 mmHg, yield 41.7%) were synthesized by the dehydrochlorination of the corresponding chlorohydrin compounds prepared by the reaction of α, β -dichloropropionaldehyde with the Grignard reagents from methyl, ethyl, propyl, butyl bromide and bromobenzene.

By the analogous procedure with the Grignard reagent from *p*-chlorostyrene in tetrahydrofuran, *p*-(3-chloro-1,2-epoxypropyl)styrene (bp 108~115°C/0.75 mmHg, yield 12%) was also obtained, and polymerized in bulk using 2,2'-azobisisobutyronitrile as an initiator to yield a reactive polymer having pendant epoxy groups.

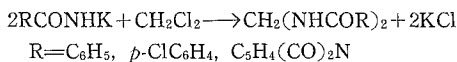
Substitution in Dimethyl Sulfoxide and Dimethylformamide. S. Tanimoto, R. Taniyasu and M. Okano. *Yuki Gosei Kagaku Kyokai Shi*, 29, 166 (1971), in Japanese.—It is well known that dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) are unique solvents for various reactions. An illustration for this was presented. Sodium phenolate and analogous compounds reacted readily at room temperature with methylene chloride in DMSO, forming the corresponding diaryl formal, as follows:



Similar reactions proceeded smoothly in DMF. Sodium phenolate and analogous compounds reacted easily with chloromethyl methyl ether in DMSO, producing the corresponding aryl methyl as follows:



As would be expected from the above results, potassium salt of benzamide and analogous compounds reacted at room temperature with methylene chloride in DMSO, forming in corresponding methylenebisamide, as follows:



Syntheses and some Reactions of β, β -dichlorovinyl Sulfones. S. Tanimoto, S. Yasuda and M. Okano. *Yuki Gosei Kagaku Kyokai Shi*, 28, 1041 (1970), in Japanese.—The syntheses and some reactions of β, β -dichlorovinyl sulfones were investigated. The condensation of arylsulfonyl chloride with vinylidene chloride followed by dehydrochlorination with the aid of triethylamine gave the following; β, β -dichlorovinyl-phenyl sulfone (mp 48~51°C), β, β -dichlorovinyl-*p*-tolyl sulfone (mp 50~53°C), β, β -dichlorovinyl-2,4-dimethylphenyl sulfone (mp 45~48°C) and β, β -dichlorovinyl-2,5-dimethylphenyl sulfone (mp 112~115.5°C).

The reaction of β, β -dichlorovinyl sulfone with aniline or with *p*-chloroaniline could be achieved, and the corresponding β, β -dianilinovinyl sulfone or β, β -di(*p*-chloroanilino) vinyl sulfone was prepared.

β, β -Di(*p*-nitrophenoxy) vinyl sulfone was also obtained by the reaction of β, β -dichlorovinyl sulfone with sodium *p*-nitrophenolate, suspended in dimethyl

sulfoxide.

Transjointing Reaction of N-Sulfomethylaniline and the Analogous Compounds.

S. Yasuda, S. Tanimoto and M. Okano. *Yuki Gosei Kagaku Kyokai Shi*, 28, 1137 (1970), in Japanese.—This paper describes the results of investigation on sodium hydroxide-catalyzed transjointing reaction of four jointed compounds by formaldehyde [N-sulfomethylaniline (SMA), *p*-chloro-N-sulfomethylaniline (*p*-CSA), N-sulfomethyl-*p*-toluidine (S-*p*-T) and N-sulfomethyl-2-naphthamide (SMN)].

Methylenebisbenzamide (MBB), methylenebis-*p*-toluamide (MB-*p*-T), 4,4'-dichloromethylenebisbenzamide (DCM), N-phthalimidomethylaniline and diindolylmethane (DIM) were obtained by the reaction between SMA and each one of benzamide, *p*-toluamide, *p*-chlorobenzamide, phthalimide or indole.

MBB, MB-*p*-T, DCM, *p*-chloro-N-phthalimidomethylaniline and DIM were obtained by the reaction between *p*-CSA and each one of benzamide, *p*-toluamide, *p*-chlorobenzamide, Phthalimide or indole.

MBB, MB-*p*-T, DCM, N-phthalimidomethyl-*p*-toluidine and DIM were obtained by the reaction between S-*p*-T and each one of benzamide, *p*-toluamide, *p*-chlorobenzamide, phthalimide or indole.

Methylenebis-2-naphthamide, MB-*p*-T, DCM, N-phthalimidomethyl-2-naphthamide and DIM were obtained by the reaction between SMN and each one of 2-naphthamide, *p*-toluamide, *p*-chlorobenzamide, phthalimide or indole.

Syntheses of Polymers Containing 1,2-Diphenoxyethane. S. Yasuda, S. Tanimoto and M. Okano. *Yuki Gosei Kagaku Kyokai Shi*, 28, 1141 (1970), in Japanese.—Syntheses of polymers using 1,2-diphenoxyethane (1) as the starting material are described. (1) was prepared in an excellent yield by the condensation of phenol with ethylene bromide in the presence of NaOH using dimethyl sulfoxide (DMSO)-H₂O medium.

1,2-Diphenoxyethane-*p,p'*-diethylene oxide (4) was obtained by the attack of sulfonium-ylid on *p,p'*-diformyl-1,2-diphenoxyethane (3), which was prepared by the condensation of *p*-hydroxybenzaldehyde with ethylene bromide.

p,p'-Dichloromethyl-1,2-diphenoxyethane (2), obtained by the dichloromethylation of (1) with formaldehyde and HCl, was converted to bisphenol (5), and (5) was converted further to polyester (6) and diglycidyl ether (7).

(2) was treated with triphenylphosphine to give quaternary phosphonium salt (10), which was reacted with (3) as an example of witting reaction.

Furthermore, polyether (8) or polysulfide (9) was synthesized by the condensation of (2) with phenolphthalein or Na₂S. *p,p'*-Dicyanomethyl-1,2-diphenoxyethane (12), derived from (2), was treated with formaldehyde to give dimethylol compound (14) and a cross-linked polymer (15).

Polyester (13) was also obtained by the reaction of (12) with 1,6-hexanediol.

Lastly, (12) was condensed with (2) in the presence of potassium tert-butoxide in tert-butyl alcohol to give a polymer (16) which has no solvent.

Synthesis of Polyamide-benzoxazoles. Y. Imazu, S. Tanimoto and M. Okano.

Yuki Gosei Kagaku Kyokai Shi, **29**, 717 (1971), in Japanese.—The solution polycondensation of 2,4-diaminophenol dihydrochloride in an inert atmosphere with adipic acid, suberic acid, azelaic acid, sebacic acid, terephthalic acid, isophthalic acid, diphenic acid and pyridine-2,4-dicarboxylic acid in polyphosphoric acid was found to give the corresponding polyamide-benzoxazoles in 42~86% yield.

Their preparations and physical properties, such as thermal stability, solubility and viscosity, were determined.

These results suggested that the polyamide-benzoxazoles with all aromatic units showed outstanding heat stability, however, the polyamide-benzoxazoles had lower thermal stability than the polyamide-benzimidazoles, although their solubilities in solvents such as dimethyl sulfoxide, N,N-dimethylformamide, *m*-cresol and formic acid were the same.

Organic Syntheses using Acrylamide. S. Tanimoto. *Yuki Gosei Kagaku Kyokai Shi*, **28**, 1266 (1970), in Japanese.—Review.

Formation of Chlorobenzene by the Reaction of Phenylthallium (III) Compounds with Copper Chloride. K. Ichikawa and Y. Ikeda. *J. Chem. Soc. (D). (Chem. Comm.)*, 169 (1971).—The reaction of phenylthallium (III) compounds with CuCl_2 and CuCl in AcOH , MeCN , and tetrahydrofuran gives mainly chlorobenzene.

Carboxylation of some Aromatic Hydrocarbons with Thallium (III) Chloride Tetrahydrate in Carbon Tetrachloride. S. Uemura, O. Sasaki and M. Okano. *J. Chem. Soc. (D). (Chem. Comm.)*, 1139 (1970).—Certain aromatic hydrocarbons react with thallium (III) chloride tetrahydrate in carbon tetrachloride to give the corresponding benzoic acids together with the expected chlorinated compounds.

1,2- and 1,4-Diacetoxylation of Conjugated Dienes with Thallium (III) and Lead (IV) Acetates. S. Uemura, A. Tabata and M. Okano. *J. Chem. Soc. (D). (Chem. Comm.)*, 1630 (1970).—The first example of 1,4-addition of acetoxygroups to conjugate dienes occurred during oxidation with Tl^{III} and Pb^{IV} acetates.

Aromatic Coupling of Arylthallium (III) Compounds by Palladium (II) Chloride. S. Uemura, Y. Ikeda and K. Ichikawa. *J. Chem. Soc. (D). (Chem. Comm.)*, 390 (1971).—In HOAc containing NaOAc arylthallium (III) compounds reacted with PbCl_2 give mainly aromatic coupled products.

Reaction of Aromatics with Thallic Salts—Preparation of Arylthallic Compounds. K. Ichikawa, S. Uemura, T. Nakano and E. Uegaki. *Bull. Chem. Soc. Japan*, **44**, 545 (1971).—Arylthallic acetate perchlorate monohydrates, $\text{Ar-Tl}(\text{OAc})(\text{ClO}_4) \cdot \text{H}_2\text{O}$, were obtained as the major products of the reaction between thallic acetate and aromatics in acetic acid containing perchloric acid. As the minor products, various types of oxidation products including oxidative coupling were

obtained. Reactivity order of the aromatics and the isomer distributions in the products were the same as those in the usual electrophilic aromatic substitution. With thallic nitrate, sulfate, and chloride, no arylthallic compounds could be obtained.

Terpenoids. Part XV. Structure and Absolute Configuration of Oridonin isolated from *Isodon japonicus* and *Isodon trichocarpus*. E. Fujita, T. Fujita, H. Katayama, M. Shibuya and T. Shingu. *J. Chem. Soc. (C)*, 1674 (1970).—Oridonin, a new diterpenoid from *Isodon japonicus* and *Isodon trichocarpus*, was shown to be *ent*-7 β , 20-epoxy-1 β , 6 α , 7 α , 14 α -tetrahydroxy-16-kauren-15-one on the basis of chemical and spectroscopic evidence.

Terpenoids. Part XVI. Chemical Conversion of Oridonin into Isodocarpin. E. Fujita, T. Fujita and H. Katayama. *J. Chem. Soc. (C)*, 1681 (1970).—Oridonin, a kaurene-type diterpenoid of *Isodon* species, was transformed into isodocarpin, a B-secokaurene-type diterpenoid from the same plant source. Dihydroenmein was also converted into enmein.

Terpenoids. XVII. Chemical Conversion of Trichokaurin into Isodocarpin via a Direct Pathway. E. Fujita, T. Fujita and Y. Nagao. *Chem. Pharm. Bull. (Tokyo)*, 18, 2343 (1970).—A chemical conversion of trichokaurin into isodocarpin via a more convenient route with much less steps compared to the previously published way was attempted and carried out with success. A potential precursor of enmein or oridonin labeled with tritium was easily prepared during this course.

A Common Stereoelectronic Requirement in Epimerisations with Some Diterpene Alcohols. E. Fujita and Y. Nagao. *J. Chem. Soc. (D). (Chem. Comm.)*, 1211 (1970).—This communication deals with a common stereoelectronic requirement in the transition state of epimerizations with some diterpene alcohols. This requirement is satisfied in the epimerization by weak alkali of the *cis*-alcohols derived from enmein into the *trans*-alcohols and also in that of the β -axial alcohol of the gibberellin series into its α -equatorial epimer.

Total Synthesis of Optically Active Natural O-Methylthalicberine. E. Fujita and A. Sumi. *Chem. Pharm. Bull. (Tokyo)*, 18, 2591 (1970).—This communication deals with a total synthesis of optically active O-methylthalicberine, a major bisbenzyl-isoquinoline-type alkaloid of *Thalictrum Thunbergii* DC. This synthesis completely confirmed and established the structure and absolute configuration of this alkaloid.

Lythraceous Alkaloids. I. Characterization of the Novel Alkaloids, Lythranine, Lythranidine, and Lythramine isolated from *Lythrum anceps* Makino. E. Fujita, K. Bessho, K. Fuji and A. Sumi. *Chem. Pharm. Bull. (Tokyo)*, 18, 2216 (1970).—Novel alkaloids, lythranine, lythranidine, and lythramine, were isolated from *Lythrum anceps* Makino. Lythranine, C₂₈H₂₇O₅N, was hydrolyzed with weak alkali

to give lythranidine, $C_{26}H_{35}O_4N$. Lythranine on reaction with formalin gave lythramine, $C_{25}H_{37}O_5N$. Functional groups were investigated on these alkaloids and all of the O- and N-functions were clarified.

Lythraceous Alkaloids. II. The Structure of O-Methyllythranidine. E. Fujita, K. Fuji, K. Bessho and S. Nakamura. *Chem. Pharm. Bull. (Tokyo)*, **18**, 2393 (1970).—Permanganate oxidation of O-methyllythranidine gave the evidence for the presence of 2, 2'-disubstituted diphenyl group in the molecule. O, N-Dimethyllythranidine was subjected to repeated Hofmann degradations followed by hydrogenations to give des-N base, which was oxidized to diketone. Subsequently, the presence of a piperidine ring in the alkaloid was proved by a series of reactions. Some reactions and nuclear magnetic resonance spectral investigations of the products led to presentation of the structure of O-methyllythranidine.

Lythraceous Alkaloids. Part III. Synthesis of the Product of Dehydrogenation of Dideoxy-NO-dimethyl-lythranidine; the Structure of Lythranidine. E. Fujita, K. Fuji and K. Tanaka. *J. Chem. Soc. (C)*, 205 (1971).—A seventeen-membered heterocycle, made from anisaldehyde by an eight-step synthesis, was shown to be identical with the product of dehydrogenation of dideoxy-NO-dimethyllythranidine. Lythranidine, a novel alkaloid from *Lythrum anceps* Makino, was thus assigned a unique structure.

Lythraceous Alkaloids. Part IV. Structure and Absolute Configuration of Lythranine, Lythranidine, and Lythramine. E. Fujita and K. Fuji. *J. Chem. Soc. (C)*, 1651 (1971).—On the basis of the specific rotation and n.m.r. data of several derivatives of lythranidine, the *trans*-relationship between C-5-H and C-9-H and between C-3-H and C-11-H was deduced. An x-ray analysis of bromolythranine hydrobromide by Sim and McClure, jun. clarified its structure and absolute configuration. Consequently, it is possible to assign the structure and absolute configurations to lythranine, lythranidine, and lythramine.

The Structures of Lythrum Alkaloids, Lythrancine-I, -II, -III, -IV, Lythrancepine-I, -II, and -III. E. Fujita and Y. Saeki. *J. Chem. Soc. (D). (Chem. Comm.)*, 368 (1971).—The structures of seven new alkaloids, lythrancine-I, -II, -III, -IV, and lythrancepine-I, -II, and -III were clarified. They have a 2, 2'-dimethoxydiphenyl part and a quinolizidine nucleus. The assignments of the structures were based on the n.m.r. spectral data and some chemical evidences.

Reaction of Allenes. IV. New Palladium Complexes Having a Bridged Allene Trimer Ligand. T. Okamoto. *Bull. Chem. Soc. Japan*, **44**, 1353 (1970).—Di- μ -acetato [2, 2'-(1-methyleneethylene) bis- π -allyl]-dipalladium (I) was obtained (18 %) by the reaction of allene and palladium acetate. Its structure was estimated from the data of elemental analysis, molecular weight, hydrogenolysis reaction, IR, and NMR. Complex I was synthesized otherwise by the reaction of allene with di- μ -acetato-2, 2'-bi- π -allyldipalladium. The insertion mechanism for the

latter reaction was confirmed by the product of the reaction using allene- d_4 , $\text{Pd}_2(\text{C}_9\text{H}_5\text{D}_4)(\text{CH}_3\text{COO})_2$. It was found that this insertion reaction was by far faster than analogous reactions with bis(acetylacetonato)-2, 2'-bi- π -allyldipalladium or di- μ -acetato-bis(π -allylpalladium). The observed acceleration was assumed to be due to strain in the substrate. From NMR data of I and other π -allylpalladium complexes already published, it was shown that the difference in chemical shifts between *syn* and *anti* protons of π -allyl complexes is dependent on the substituents on the central carbons; the nonconjugated substituents give smaller values (0.9-1.01 ppm for μ -chloro complexes), and α , β -unsaturated substituents give larger values (1.27-1.28 ppm for μ -chloro complex). Chloro and acetylacetonato derivatives of I, and the activation energy for spin exchange of saturated methylene protons in I are also described.

The Synthesis of Methylacetylene by the Pyrolysis of Propylene. VI. The Pyrolysis of Allyl Iodide. S. Kunichika, Y. Sakakibara and M. Taniuchi. *Bull. Chem. Soc. Japan*, 44, 1388 (1971).—Allyl iodide has been pyrolyzed in a flow system over a wide range of conditions (temperature, 800-1100°C; contact time, 144×10^{-4} – 14.0×10^{-4} sec; concentration, 1.8-6.5 mol %; pressure, atmospheric pressure) in order to find suitable condition for producing methylacetylene and allene and in order to elucidate the reactions of the allyl radical with iodine atom at high temperatures. In addition, a study of the mechanism of the pyrolysis of allyl iodide at high temperatures (800-1100°C) has been made. A total yield of allene and methylacetylene of 10 mol per 100 mol of allyl iodide pyrolyzed was obtained under suitable conditions. In the pyrolysis, little cleavage of the C-C bonds of allyl iodide occurred, and propylene, allene, methylacetylene, diallyl, benzene, and an unidentified product were found to be the main products. By means of the zero-conversion method, diallyl alone has been found to be the major product in the early stage of the pyrolysis, while propylene, allene, methylacetylene, and benzene have been found to be the chief products at higher conversions. On the basis of the observed results, a free-radical mechanism has been proposed for the main reactions. It has further been concluded that the pyrolysis is a radical decomposition initiated by the $\text{C}_3\text{H}_5\text{I} \rightarrow \text{C}_3\text{H}_5\cdot + \text{I}$ reaction and that the overall mechanism in the early stage of the pyrolysis may be represented essentially by the $2\text{C}_3\text{H}_5\text{I} \rightarrow \text{C}_6\text{H}_{10} + \text{I}_2$ reaction.

Ready Insertion of Allene into Di- μ -acetato-2, 2'-bi- π -allyldipalladium. T. Okamoto. *J. Chem. Soc. (D) (Chem. Comm.)*, 1126 (1970).—The title reaction readily gave a product, $\text{Pd}_2(\text{C}_9\text{H}_{12})(\text{OAc})_2$, which suggests that strain in the complex assists the insertion reaction.

Friedel-Crafts Rearrangements of 1, 2-Ditolylethanes. S. Kunichika, S. Oka, T. Sugiyama, C. Inoue and M. Ichii. *Nippon Kagaku Zasshi*, 92, 539 (1971).—The isomerization of 1, 2-ditolylethanes (DTE) with AlBr_3 HBr has been investigated at 50°C in toluene. In each case the samples were periodically taken out from the reaction mixture and analyzed by vapor phase chromatography. Every

equilibrium isomer mixture obtained from any of *o*, *o'*-, *m*, *m'*-, and *p*, *p'*-isomers as a starting material contains about 42 % *m*, *m'*-, 35 % *m*, *p'*-, 12 % *o*, *m'*-, 7 % *p*, *p'*-, and 4 % *o*, *p'*-DTE together with a trace of *o*, *o'*-isomer. Under the same conditions, 1, 2-diphenylethane in toluene was slowly converted into 1-phenyl-2-tolyethanes and DTE with several constant distributions of the isomers. These results suggest that the isomerization proceeds more rapidly by an intramolecular 1, 2-shift than by an intermolecular mechanism.

Polymer Chemistry

Viscoelastic Properties of Polymer Solutions in High-Viscosity Solvents and Limiting High-Frequency Behavior. I. Polystyrene and Poly (α -methylstyrene). K. Osaki and J. L. Schrag. *Polymer J.*, 2, 541 (1971).—Storage (G') and loss (G'') moduli were measured for dilute solutions of polystyrene (PS) and poly (α -methylstyrene) (PMS) in Aroclor (chlorinated diphenyl) with the modified Birnboim transducer. The molecular weights (M) were 5.1×10^4 , 8.2×10^4 , and 2.67×10^5 for PS and 3.55×10^5 and 8.7×10^5 for PMS, and the ranges of concentration (c) were 1.5×10^{-2} to 7.6×10^{-2} g/ml for PS and 1.5×10^{-2} to 4.6×10^{-2} for PMS, respectively. The solvent viscosity η_s varied from 5000 to 9.3 poise over the temperature range of 10 to 35°C employed. The frequency range was 0.02 to 630 Hz. The limiting value of the dynamic viscosity at high frequency η_{∞}' is described by an equation $\ln(\eta_{\infty}'/\eta_s) = [\eta']_{\infty} c$ over the whole range of concentration, where $[\eta']_{\infty}$ is a constant independent of M and is 14.3 and 22.2 ml/g for PS and PMS, respectively. The limiting value of G' at high frequency is approximately proportional to c . The time-temperature reduction rule was successfully applied to G' and $G'' - \omega\eta_s$ and the shapes of frequency dependence curves of the reduced moduli were described well by the theory of Peterlin.

Stress Relaxation of Polymer Solutions under Large Strain. Y. Einaga, K. Osaki, M. Kurata, S. Kimura and M. Tamura. *Polymer J.*, 2, 550 (1971).—The stress relaxation behavior of polymer solutions was studied under large torsional strain in the gap of a cone-plate type apparatus. The measurements were performed on a 20 % of narrow-distribution polystyrene in chlorinated diphenyl at 33.5°C. It was found that the relaxation moduli became strain-dependent as the strain was increased beyond about 2 strain units, but the terminal relaxation time remained unaffected. The stress relaxation curves obtained under various strains were superposable on a composite curve by the vertical shift, except for their short time portions. The shift factor was found to be proportional to the 0.83 power of the first invariance of the strain tensor.

Irreversible Statistical Mechanics of Polymer Chains. I. Fokker-Planck Diffusion Equation. K. Iwata. *J. Chem. Phys.*, 54, 12 (1971).—A theory of the irreversible statistical mechanics of flexible polymer chains is developed on the basis of new ideas. The Brownian motion of polymer chains is assumed to be a Markoff random transition among their rotational isomeric states. The theory

is described for ring polymer chains, for which the "normal coordinates" can be determined by the consideration of their symmetry alone. First, we derive the master equation which describes the discrete Brownian motion of a ring polymer chain. The master equation is averaged over all the configurations, fixed several normal coordinates to certain values. This averaging process is called "coarse graining." By Taylor expansion of the coarse-grained master equation, we get a Fokker-Planck diffusion equation which is specified by two kinds of molecular constants, the diffusion constant D_α and the expansion parameter r_α , both of which depend on the suffix α of the normal coordinates. For slow relaxation phenomena, the diffusion equation is reduced to that of the spring-bead model theory. The general behaviors of D_α and r_α are discussed: The reduced diffusion constant $D_\alpha (= D_\alpha/D_0)$ decreases rapidly as α increases, whereas r_α^2/α^2 remains roughly constant.

Irreversible Statistical Mechanics of Polymer Chains. II. Viscosity. K. Iwata. *J. Chem. Phys.*, 54, 1570 (1971).—The Fokker-Planck diffusion equation derived in the previous paper is applied to Erpenbeck-Kirkwood theory on the viscosity of polymer solutions. The Newtonian viscosity for ring polymers is given by

$$\eta N = 2ckT \sum_{\sigma=1}^N \tau_\sigma / (1 + i\omega\tau_\sigma),$$

where τ_σ is the relaxation time, c is the number of polymers in unit volume, and kT has the usual meaning. Without hydrodynamic interactions among monomer units, the relaxation time is given by

$$\tau_\sigma = r_\sigma^2 / 2D_\sigma,$$

where r_σ and D_σ are, respectively, the expansion parameter and the diffusiton constant in regard to the normal coordinate Q_σ . With hydrodynamic interactions, the relaxation time is modified as

$$\tau_\sigma' = \tau_\sigma (1 + kT\tilde{T}_\sigma / D_\sigma),$$

where \tilde{T}_σ is the σ th eigenvalue of Kirkwood-Riseman tensor.

Creep Behavior of Polymer Solutions. I. A New Type of Apparatus for Creep and Creep Recovery. K. Osaki, Y. Einaga, M. Kurata and M. Tamura. *Macromolecules*, 4, 82 (1971).—A new type of apparatus was devised for measuring the creep as well as the creep recovery of a viscoelastic material whose viscosity lies between 10^4 and 10^8 P. The apparatus is very similar to the torsion creep apparatus of Plazek, but is simpler in design. The torsion wire is suspended by a thin thread at its top. The measurement of creep recovery is performed at the end of the creep measurement by releasing the torque due to the twist of the torsion wire on the thread. A brief review of various existing methods of determination of the steady-shear compliance is given, and the need for obtaining unambiguous results in measurement of creep recovery and for elucidating the slow deformation characteristics of polymer solutions is emphasized.

Creep Behavior of Polymer Solutions. II. Steady-Shear Coppliance of Con-

concentrated Polystyrene Solutions. Y. Einaga, K. Osaki, M. Kurata and M. Tamura. *Macromolecules*, **4**, 87 (1971).—The steady-shear compliance J_e and the viscosity η were measured on concentrated solutions of narrow distribution polystyrene in chlorinated diphenyl with a new type of apparatus for measurement of creep and creep recovery. The range of molecular weight studied was $9.7 \times 10^4 \sim 1.8 \times 10^6$ and that of concentration was 0.1×0.6 g/ml. The steady-shear compliance first increased with increasing concentration c , reached a maximum, and then decreased in proportion to c^{-3} . J_e was independent of molecular weight in the range of high concentration where it was proportional to c^{-3} . The maximum in J_e was lower and appeared at higher concentration if the molecular weight was lower. The concentration above which J_e obeyed the c^{-3} dependence was higher for lower molecular weight. The viscosity η was proportional to $M^{3.4}$ in the whole range of concentration. Thus, the entangled system for which the viscosity is proportional to the 3.4th power of molecular weight is further divided into two classes according to the behavior of J_e . Only in the highly entangled state does J_e become proportional to c^{-3} and independent of M . The assumption of uniform excess friction in the modified Rouse theory is not applicable to this highly entangled state of polystyrene.

Shear Creep Studies of Narrow-Distribution Poly (*cis*-isoprene). N. Nemoto, M. Moriwaki, H. Odani and M. Kurata. *Macromolecules*, **4**, 215 (1971).—Shear creep measurements were made at temperatures between -68.6 and 98.0° on six narrow-distribution poly(*cis*-isoprene) samples with molecular weights of 57,600–1,120,000. The time-temperature reduction method was used for constructing master Curves at a reference temperature of -30° . The curves for two low molecular weight samples ($M_w=57,600$ and $103,000$) showed deviations in the transition zone from those for other samples with higher molecular weights. Also, a corresponding effect of low molecular weight was observed on the shift factor a_T . It was found that these effects were avoided by the use of a lower value for the reference temperature of the samples. The viscosity η and the steady-state compliance J_e were determined by the extrapolation method of Nino-miya. Also the maximum relaxation time, τ_m , was evaluated by procedure X. It was found that η and τ_m varied as a power of the molecular weight, $M^{3.4}$, and J_e was independent of M . These results were in qualitative agreement with Hayashi's theory and also with Graessley's theory for entanglements. The entanglement spacing M_e was about 3500 and was nearly independent of M determined from the inflection in the $J(t)$ curves.

Fluorescence Depolarization in Sheared Solutions of Dye-tagged Polymers. S. Claesson and H. Odani. *Disc. Faraday Soc.*, **49**, 268 (1970).—The micro-Brownian motion of a polymer chain in sheared solutions has been studied by means of fluorescence depolarization. An apparatus for determining the degree of polarization of sheared solutions was designed, and measurements were made on fluorescein in aqueous hydroxyethyl cellulose solutions, both tagged to the polymer chains and freely dispersed. The degree of polarization was independent of rate

of shear in the region studied, $0\text{--}10^4\text{s}^{-1}$, though the flow viscosity of the solutions showed marked non-Newtonian nature. Similar behaviour was observed for concentrated solutions of dextran and polystyrene.

Sedimentation Equilibrium in Nonideal Heterogeneous Systems. I. Fundamental Equations for Heterogeneous Solute Systems and Some Preliminary Results. T. Kotaka, N. Donkai and H. Inagaki. *J. Polymer Sci., A-2*, **9**, 1379 (1971).—The sedimentation equilibrium method is extended to treat nonideal solutions of heterogeneous macromolecules. The solute is assumed to be heterogeneous not only in molecular weight but also in other quantities such as partial specific volume, second virial coefficient and specific refractive increment. General expressions for various observable molecular weights, especially giving a type of weight-average, z -average and number-average molecular weight, are derived. Their dependences on sedimentation parameter and solute-concentration are discussed in detail. For the extrapolation of observable molecular weights, giving a type of weight-average and z -average, to infinite dilution to estimate the molecular weight and the second virial coefficient, use of average concentration as a concentration variable is superior to that of original concentration. The plots of observable molecular weight versus average concentration are usually less influenced by the choice of the sedimentation parameter, especially of rotor speed.

The general expressions are applied to a few special cases, monodisperse polymer, polydisperse homologous polymer and polymer blend. The results are compared with experiments on a monodisperse polystyrene, a polydisperse poly(methyl methacrylate) and a mixture of the two polymers, all in 2-butanone at 25°C . The agreement between the theory and experiments is satisfactory.

Dilute Solution Behavior of Block Copolymers: Styrene-Methyl Methacrylate and α -Methyl Styrene-Methyl Methacrylate Systems. T. Kotaka, H. Ohnuma and H. Inagaki. “*Colloidal and Morphological Behavior of Block and Graft Copolymers*” (Ed. by G. E. Molau), P. 259, Plenum Press, New York, London, 1971.—The solution properties of block copolymers, particularly in relation with the incompatibility of corresponding ternary systems, are examined. Pairs of styrene (ST) with methyl methacrylate (MMA) and of α -methyl styrene (MST) with MMA are chosen, since PST and PMMA are known to be an incompatible pair, whereas PMST and PMMA are exceptionally a compatible pair.

The following conclusions are drawn: (i) Block copolymer chains (of any architecture) would behave just as ordinary random coils in dilute solution of common solvents, unless the parent homopolymer pair is highly incompatible. Of course if the homopolymer pair is highly incompatible, it should be difficult to find appropriate common solvents. (ii) Block copolymers of AB-type would become ‘soluble’ in dilute solution of any selective solvents, *i.e.*, that dissolve either one of the constituent homopolymers, presumably by forming micelles. The insoluble subchains accumulate in the cores of such micelles, while the soluble subchains wrap around the cores and protect them from further aggregation. On the other hand, the behavior of BAB triblock copolymers may be more

easily influenced by the selectivity of solvents. Namely (iii) in a nonsolvent of A subchains, a single block copolymer molecule can be a micelle particle, in which insoluble central A subchain is protected by soluble B side chains. The solvent becomes much poorer, they may form intermolecular aggregates. On the contrary (iv) in a solvent of the opposite selectivity, *i.e.*, in a nonsolvent of B subchains, BAB triblock copolymers are usually insoluble. Even when they are in the state of molecular dispersion, the insoluble B subchains would undergo intrachain association within the same molecule, thereby restricting allowable conformations of the central A subchain. (v) The stability of the micelles including the unimolecular dispersion of BAB triblock chains appears to be better for block copolymers composed of incompatible homopolymer pair rather than those of compatible homopolymer pair. (vi) Of course the detailed features should be influenced by many other factors such as the molecular weight and composition of the block copolymers.

The Width of the Molecular Weight Distribution of a Polymer as Determined by Density Gradient Centrifugation. A. Nakazawa and J. J. Hermans. *Koninkl. Nederl. Akademie van Wetenschappen-Amsterdam*, B 73, 334 (1970).—The schlieren curves obtained in the equilibrium density gradient centrifugation of a polystyrene sample is used to calculate the ratio M_w/M_n . The solvent used is a mixture of benzene, bromoform and nitromethane, which is found to be a theta solvent for polystyrene at 26°C. The M.W. averages are derived from moments of the polymer distribution. The result of extrapolating to zero polymer content is independent of whether the M.W. averages or their ratios are extrapolated, and leads to the impossible value 0.9 for M_w/M_n , which lies about 10 % below the expected value. A closer analysis of the theory of density gradient centrifugation reveals a possible source of this error, but shows also that no simple procedure for correcting the error can be developed.

A Note on Fractionation of Polymers by Thin Layer Chromatography. H. Inagaki, F. Kamiyama and T. Yagi. *Macromolecules*, 4, 133 (1971).—The mechanism of thin layer chromatographic fractionation of polymeric substances by molecular weight is studied with fractions of poly(methyl methacrylate) having different molecular weight, and mixtures of chloroform and ethanol as developer. Distinct molecular weight dependences of R_f (rate of flow) in the range of higher molecular weights, *e.g.*, 10^5 were observed for developers that behave as poor solvents or precipitants for polymer, while those almost disappeared for developers that dissolve well the polymer. This result implies that the mechanism due to phase separation of polymer dictates efficient polymer fractionation.

Determination of Molecular Weight Distribution of Polymeric Substances by Thin-Layer Chromatography. F. Kamiyama, H. Matsuda and H. Inagaki. *Polymer Journal*, 1, 518 (1970).—Thin-layer chromatography (TLC) combined with concentration gradient development has been applied to the determination of the molecular weight distribution of polystyrene prepared by a radical polymerization.

Developers obtained by mixing polar nonsolvents with moderately good solvents toward polystyrene were found to give complete separation of polymer according to molecular weight. It was proved that the molecular weight distribution deduced from the present TLC experiment was in good agreement with that from a gel-permeation chromatography experiment.

Thermodynamic and Conformational Properties of Styrene-Methyl Methacrylate Block Copolymers in Dilute Solution. III. Viscometric Behavior in Relation to Incompatibility of Parent Homopolymers. H. Ohnuma, T. Kotaka and H. Inagaki. *Polymer Journal*, 1, 716 (1970).—Viscometric behavior of nearly equimolar block copolymers of the poly(methyl methacrylate)-polystyrene-poly(methacrylate) type are studied in various solvents. The behavior is discussed in relation to the incompatibility of the parent homopolymers in each solvent. A correlation is found between the excluded-volume interactions in the block copolymer chain and the incompatibility of the homopolymer pair. A high compatibility is observed for the pair in cyclohexanol, and this reinforces our previous argument that this solvent may provide a genuine θ condition for the block copolymer, wherein random-flight statistics prevails. In certain common solvents, the homopolymer pair is fairly compatible, and the viscometric behavior of the block copolymer shows no anomalies: the so-called phenomenon of intrachain phase separation is unlikely to be taking place in such solvents. In θ solvents for either one of the homopolymers, they become less compatible. Nevertheless in a θ solvent for polystyrene the block copolymer shows no anomalies. On the other hand, in θ solvents for poly(methyl methacrylate), significant anomalies are observed. The anomalies must be due to the triblock architecture of the block copolymer chains: the two poly(methyl methacrylate) side-chains undergo intrachain association, thereby restricting allowable conformations of the central polystyrene chain.

Biochemistry

Effects of Pressure on ATPase of Myosin A, Heavy Meromyosin, and Subfragment I. T. Ikkai and T. Ooi. *Biochim. Biophys. Acta*, 234, 190 (1971).—The effect of pressure on the ATPase of myosin A, heavy meromyosin, and Subfragment I was investigated¹ over a pressure range from 1 atm to 2200 kg/cm². In the presence of Ca²⁺, the ATPase activity of myosin A, heavy meromyosin, and Subfragment I was first enhanced and then depressed by the increase in pressure, having a maximum at about 1000 kg/cm². The optimal pressure for activation and the extent of the activation increased with increasing salt concentration². When the pH of a solution containing Ca²⁺ was changed, the ATPase activity of heavy meromyosin and Subfragment I at 1300 kg/cm² had a maximum around pH 8 in Tris-HCl and borate-KOH buffers. After the correction of the pH of the buffers under pressure by use of pH indicators (0.3 pH unit for Tris-HCl and -0.2 unit for borate-KOH buffer at 1300 kg/cm²), the maximal activation was found at pH 8.1 in both buffers³. In contrast with the activation of the Ca²⁺-activated

ATPase, the EDTA-activated ATPase of heavy meromyosin and Subfragment I was depressed by pressure in the same way as it was depressed by *p*-chloromercuribenzoate⁴. These effects of pressure, especially depression, were not due to any irreversible process, because the original activity was recovered after the release of pressure⁵. The pressure effects on the ATPase were analysed according to the Michaelis-Menten equation. As a result, it is inferred that pressure has effects on both the binding of the substrate and the splitting of ATP.

Biochemical Evidence for Identical Primary Structure of P-Filament and Flagellin. H. Hotani, T. Ooi, H. Kagawa, S. Asakura and S. Yamaguchi. *Biochim. Biophys. Acta*, **214**, 207 (1970).—1. A membrane fraction derived from deflagellated cells of *Salmonella* promotes polymerization of flagellin into "P-filaments" (ref. 1). The present study was undertaken to investigate whether or not changes in primary structure of flagellin are prerequisite to this polymerization.

2. In this study we used the "soluble fraction" instead of "membrane fraction" for the initiation of polymerization². Isotope experiments showed that with addition of the soluble fraction more than 90 % of the total flagellin polymerizes into P-filaments.

3. Quantitative analysis of amino terminal residues showed that polymerization is not associated with cleavage of peptide bonds in flagellin.

4. P-filament and intact flagellin were compared as to amino acid composition, amino and carboxyl terminal residues and tryptic peptide map; in these respects they were indistinguishable.

5. From these experimental results, it was concluded that the primary structure of flagellin remains unchanged after polymerization into P-filament.

Structure of Tropomyosin and Its Crystal. T. Ooi and S. Fujime-Higashi. *Advan. in Biophys.*, **2**, 113 (1971).—Tropomyosin, one of the major components of muscle proteins, has a role in the control of muscle contraction. The protein extracted from minced muscle with a concentrated salt solution is polymerizable at a low ionic strength. Physicochemical studies on polymerization-depolymerization properties indicate that molecules with a rod-like shape interact with each other not only end-to-end but side-by-side. The monomeric unit has a molecular weight of about 60,000 and a rod-like shape of 400 Å in length. A high helical content is consistent with the rod-shape. However biochemical studies using limited proteolysis with trypsin show that there are some loose region(s) which are easily attacked by the enzyme. Electron microscopic observations of tropomyosin crystals give information on the molecular structure which seems to be a coiled-coil of two α -helices. Binding of other proteins, especially troponin to tropomyosin, can be seen on the crystal. Finally, a possible structure of the tropomyosin molecule is discussed.

The Behaviour of the Copolymer of L-Proline and O-Benzyl-L-Tyrosine in a *n*-Propanol and Water System. T. Iio and S. Takahashi. *Bull. Chem. Soc. Japan*, **43**, 3853 (1970).—A copolymer consisting 95.8 % of L-proline and 4.2 % of O-benzyl-

L-tyrosine was transformed in conformation from Form I to Form II as the propanol content changed from 100 % to 74 %. In Form I, the copolymer took a rod-like structure like that of poly-L-proline Form I, and the O-benzyl-L-tyrosyl residue moved independently of the molecular motion of the copolymer. On the other hand, the copolymer became flexible in Form II and the components associated with each other, forming an amorphous aggregation, when the propanol content decreased further, below the transition point. The hydrophobic interaction between the O-benzyl-L-tyrosyl side chain and the prolyl residue was the main factor which made the components of the copolymer associate with each other and form an amorphous aggregation. This was verified by a fluorescence study of the O-benzyl-L-tyrosyl residue.

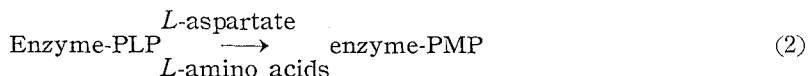
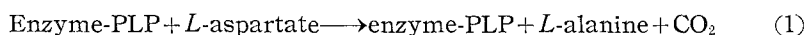
Calculation of the pK_a Values of Alcohols from Constants and from the Carbonyl Frequencies of Their Esters. S. Takahashi, L. A. Cohen, H. K. Miller and E. G. Peake. *J. Org. Chem.*, **36**, 1205 (1971).—As an alternative to direct measurement, the pK_a values of primary alcohols (RCH_2OH) may be calculated from σ^* constants by use of the equation $pK_a(RCH_2OH) = -1.316 \sigma^*(R) + 15.74$ for alcohols in which C-2 is sp^3 or sp hybridized. For those alcohols in which C-2 is sp^2 hybridized, $pK_a(RCH_2OH) = -1.316 \sigma^*(R) + 16.23$. Values of σ^* are based on pK_a data for the corresponding carboxylic acids ($RCOOH$) or on the carbonyl stretching frequencies of esters of RCH_2OH . Frequencies can be related to σ^* by bonding type: for C-2 (sp^3 or sp^2), $\sigma^*(R) = 0.08996 \nu - 156.000$; for C-2 (sp), $\sigma^*(R) = 0.11757 \nu - 203.991$; for C-2 (sp^3) but $R = \text{H or alkyl}$, $\sigma^*(R) = 0.10828 \nu - 188.316$. For secondary alcohols, pK_a values can be calculated from σ^* , the latter values being obtained by use of the additivity principle or from carbonyl frequencies of esters. Measurement of carbonyl frequency offers a novel and facile method for determination of σ^* values.

Arginine Racemase (*Pseudomonas graveolens*). K. Soda, T. Yorifuji and K. Ogata. *Methods in Enzymology*, **17-A**, 341 (1970).—This communication deals with assay method, purification procedure and characterization of arginine racemase.

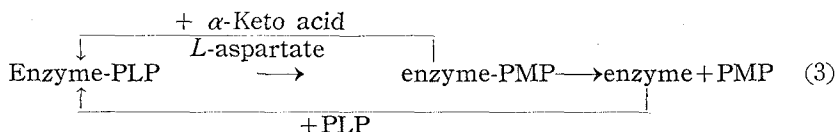
Arginine racemase catalyzes the conversion of either *D*- or *L*-arginine to the racemate. The assay method is based on the measurement of *L*-arginine formed from the *D* isomer which is used as a substrate. *L*-Arginine is determined by measuring the formation of urea released by arginine according to a slight modification of the method of Archibald. The enzyme was purified to homogeneity from the crude extract of *Pseudomonas graveolens* by ammonium sulfate fractionation, butanol treatment, DEAE-cellulose column chromatography, Sephadex G-150 column chromatography and DEAE-Sephadex column chromatography, and crystallized. The crystals appear as light yellow needles. The sedimentation coefficient and molecular weight are 5.2 S and 167,000, respectively. The enzyme exhibits absorption maxima at 280 and 420 m μ with an absorbance ratio of 5:1 and contains 4 moles of pyridoxal 5'-phosphate per mole of enzyme as a coenzyme. This amino acid racemase also catalyzes the racemization of several amino acids other than arginine, *e. g.*, lysine, ornithine, homoarginine, ethionine and threo-

nine. The arginine racemase is inhibited by hydroxylamine and L-ornithine.

L-Aspartate- β -Decarboxylase (*Alcaligenes faecalis*). S. S. Tate, A. Novogrodsky, K. Soda, E. W. Miles and A. Meister. *Methods in Enzymology*, 17-A, 681 (1970).—This enzyme, which catalyzes the β -decarboxylation of L-aspartate to L- α -alanine, has been found in a number of microorganisms. Studies on the aspartate- β -decarboxylase of *Clostridium welchii* (*perfringens*) first showed that this enzyme is markedly activated both by pyridoxal 5'-phosphate and by any of a large number of α -Keto acids. Such activation, which is also characteristic of the aspartate β -decarboxylases that have been obtained from other bacterial sources, was explained by studies on the aspartate β -decarboxylase of *Alcaligenes faecalis*, which demonstrated that this enzyme also exhibits relatively nonspecific L-amino acid transaminase activity. Although the rate of the latter reaction is equantitatively low (as compared to the rate of decarboxylation), it is of considerable significance since the transaminase reaction can destroy (or regenerate) the enzyme-bound cofactor required for the β -decarboxylation of aspartate:



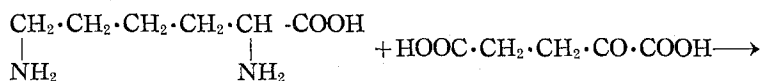
The pyridoxamine 5'-phosphate form of the enzyme dissociates readily under certain conditions to yield pyridoxamine 5'-phosphate and the apoenzyme. Thus, the observed activation by pyridoxal 5'-phosphate and α -Keto acids may be explained by the following scheme:

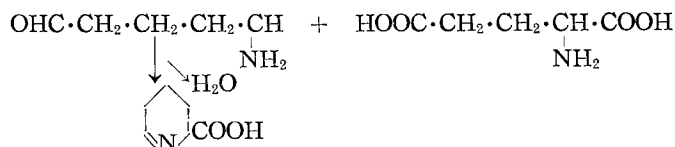


Under conditions in which there is relatively little tendency of pyridoxamine 5'-phosphate to dissociate from the enzyme, α -Keto acid will activate more than pyridoxal 5'-phosphate. Conversely, if the pyridoxamine 5'-phosphate dissociates rapidly, activation by added pyridoxal 5'-phosphate may be greater than that found after adding α -Keto acid.

L-Lysine- α -Ketoglutarate Aminotransferase (*Achromobacter liquidum*). K. Soda and H. Misono. *Methods in Enzymology*, 17-B, 222 (1971).—The assay method, purification procedure, and properties of L-Lysine- α -Ketoglutarate aminotransferase of *Achromobacter liquidum* are described in the present paper.

L-Lysine- α -Ketoglutarate aminotransferase catalyzes the transfer of the ϵ -aminogroup of L-lysine to α -Ketoglutarate to yield L-glutamate and α -aminoadi-pate- δ -semialdehyde which is immediately converted to the intramolecularly dehydrated and cyclized form, Δ^1 -piperidine-6-carboxylic acid as follows.





The assay method is based on the measurement of glutamate or Δ^1 -piperidine-6-carboxylic acid formed. The enzyme was purified to homogeneity from the cell extract of *Achromobacter liquidum* by DEAE-cellulose column chromatography, heat treatment, ammonium sulfate fractionation and hydroxylapatite column chromatography, and crystallized by addition of ammonium sulfate. The sedimentation coefficient and molecular weight of the enzyme were determined 6.37S and 116,000, respectively. The enzyme prepared freshly exhibits absorption maxima at 280, 340 and 415 m μ , and contains 2 moles of pyridoxal 5'-phosphate per mole of enzyme. An inactive form of enzyme that can be reactivated with pyridoxal 5'-phosphate or pyridoxamine 5'-phosphate is obtained by treatment of the holoenzyme with the amino donor. The inactive form of enzyme contains still 1 mole of pyridoxal 5'-phosphate per mole of enzyme and exhibits the absorption maximum at 340 m μ . This inactive form of enzyme is designated "semiapo enzyme". In addition to *L*-lysine, *L*-ornithine and S-(β -aminoethyl)-*L*-cysteine serve as the amino donor. The optimum pH for the enzyme activity is found to be 8.3 to 8.5. δ -Aminovalerate, δ -Hydroxylysine and O-(2-aminoethyl)-*DL*-serine inhibit the transaminase reaction competitively against *L*-lysine.

Amino Acid Racemase (*Pseudomonas striata*). K. Soda and T. Osumi. *Methods in Enzymology*, 17-B, 629 (1971).—The assay methods, purification procedure and properties of amino acid racemase are presented in this paper.

Amino acid racemase catalyzes the conversion of either D- or L-amino acids to the racemates. All assay methods are based on the measurement of one stereoisomer of the substrate. The enzyme was purified to homogeneity from the cell-free extracts of *Pseudomonas striata* by ammonium sulfate fractionation, DEAE-cellulose chromatography and Sephadex G-200 chromatography and crystallized by addition of ammonium sulfate.

The sedimentation coefficient and molecular weight are 4.45 S and 110,000, respectively. The enzyme exhibits absorption maxima at 280 and 420 m μ . Treatment of the enzyme with 10⁻² M hydroxylamine solution (pH 7.0) results in the formation of apoenzyme. The apoenzyme does not have an absorption maximum at 420 m μ , and can be reactivated by addition of pyridoxal 5'-phosphate. The holoenzyme contains 2 moles of pyridoxal 5'-phosphate per mole of enzyme.

The substrate specificity of the enzyme is extremely low in comparison with usual amino racemases. Optimum activity is found at 7.5 to 8.5 for all the substrates. The enzyme activity is inhibited by D-cycloserine and hydroxylamine.

L-Lysine Decarboxylase (*Bacterium cadaveris*). K. Soda and M. Moriguchi. *Methods in Enzymology*, 17-B, 677 (1971).—The present communication described purification procedure and enzymological properties of L-lysine decarboxylase of *Bacterium cadaveris*.

L-Lysine decarboxylase catalyzes the decarboxylation of L-lysine to yield cadaverine and carbon dioxide. The enzyme activity is followed by the manometric measurement of carbon dioxide released from L-lysine. The enzyme was purified to homogeneity from the crude extract of *Bacterium cadaveris* by heat treatment, ammonium sulfate fractionation, DEAE-Sephadex column chromatography, Sepharose 4B column chromatography and crystallization.

The sedimentation coefficient and molecular weight of the enzyme are 21.1 S and 1,000,000, respectively. The spectrum of the enzyme exhibits two absorption maxima at 280 and 425 m μ with an absorbance ratio of 12:1. In addition to L-lysine, δ -hydroxylysine and S-(2-aminoethyl)-L-cysteine are decarboxylated by the enzyme. The enzyme has a maximum activity at pH 5.8. The enzyme activity is markedly inhibited by *p*-chloromercuribenzoate, iodoacetamide, semicarbazide, isoniazid, hydroxylamine and mercuric chloride.

The Starting Nucleotide Sequences and Size of RNA Transcribed *In Vitro* on Phage DNA Templates. M. Takanami, T. Okamoto and M. Sugiura. *Cold Spring Harbor Symp. Quant. Biol.*, 35, 179 (1970).—The species of RNA transcribed *in vitro* on phage DNA templates by *E. coli* RNA polymerase were characterized. Several species of RNA with unique, but different, starting sequences and size were synthesized on each template. With enzyme lacking “sigma” factor the starting sequences and size of RNA became heterogeneous. The addition of “rho” caused the decrease in size of some RNA species. Possible implications of the results to the initiation and termination of RNA transcription were discussed.

Electron Microscopy of the Replicative Form DNA of Coliphage fd. T. Oda, T. Nakamura, S. Watanabe and M. Takanami. *J. Electron Microscopy*, 20, 67 (1971).—The doubly closed replicative form DNA (RF-I DNA) was purified from *E. coli* cells infected with fd, and nick(s) were introduced by treatment with DNase (RF-II DNA). Electron micrographs of RF-I DNA showed twisted circles and RF-II DNA extended circles. The mean value of the contour length of RF-II DNA was $1.84 \mu \pm 0.07 \mu$, which corresponds to a molecular weight of $3.5 \times 10^6 \pm 0.13 \times 10^6$ daltons.